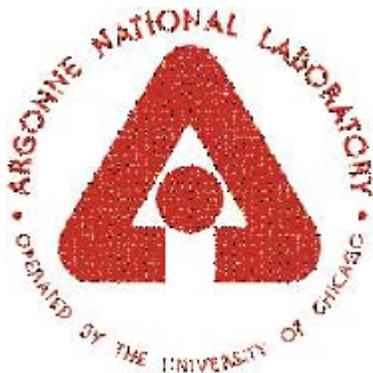


# *Catalysts for autothermal reforming*

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Hydrogen, Fuel Cells, and  
Infrastructure Technologies  
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# Objectives

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- Develop advanced autothermal reforming (ATR) catalysts that meet DOE targets for the Fast Start reformer
  - ✓ gas-hourly space velocity (GHSV)  $\geq 200,000 \text{ h}^{-1}$
  - ✓ efficiency of  $\geq 99.9\%$  with  $\text{H}_2$  selectivity of 80%
  - ✓ durability of  $\geq 5000 \text{ h}$
  - ✓ cost of  $\leq \$5/\text{kwe}$
- Develop a better understanding of reaction mechanisms to
  - ✓ increase catalytic activity
  - ✓ reduce deactivation
  - ✓ improve sulfur tolerance

This work addresses technical barriers I, J, K, and N.

# Approach

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- Building on past ANL experience, we are investigating two classes of materials.
  - ✓ Transition metal(s) supported on mixed oxide substrates
  - ✓ Perovskites, with no precious metals
- Determine catalyst performance ( $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$ ) as a function of:
  - ✓ catalyst composition
  - ✓ fuel composition and sulfur content
  - ✓ operating parameters:  $\text{O}_2$ :C and  $\text{H}_2\text{O}$ :C ratios, temperature, GHSV
- Conduct catalyst characterization and mechanistic studies to gain insight into reaction pathways.
- Work with catalyst manufacturers to optimize catalyst structure and performance.

# Industry and University collaborations

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- Industry
  - ✓ **Süd-Chemie, Inc.**
    - Manufactures catalyst under a non-exclusive licensing agreement
    - ANL and Süd-Chemie working jointly to improve catalyst structure and performance
- Universities
  - ✓ **University of Alabama (Profs. Ramana Reddy and Alan Lane)**
    - Characterization studies (SEM, TEM, XPS) of ATR catalysts
    - Kinetic and mechanistic studies of ATR catalysts
  - ✓ **University of Puerto Rico, Mayagüez (Prof. José Colucci)**
    - Determine reaction condition boundaries for carbon formation

# Reviewer's comments from FY2002 Annual Review

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- Space velocities are still low.

*We have increased the GHSV by a factor of ~4 compared to data presented at last year's review.*

- Non-CH<sub>4</sub> hydrocarbon outlet levels seem high.

*Hydrocarbon slip has been significantly reduced. We are investigating the effect of support geometry (cell density for monoliths and monolith vs. foam) to further reduce slip.*

- Demonstrating sulfur tolerance is key.

*Has proven to be challenging. Deactivation but not complete loss of activity has been observed over 100-150 h.*

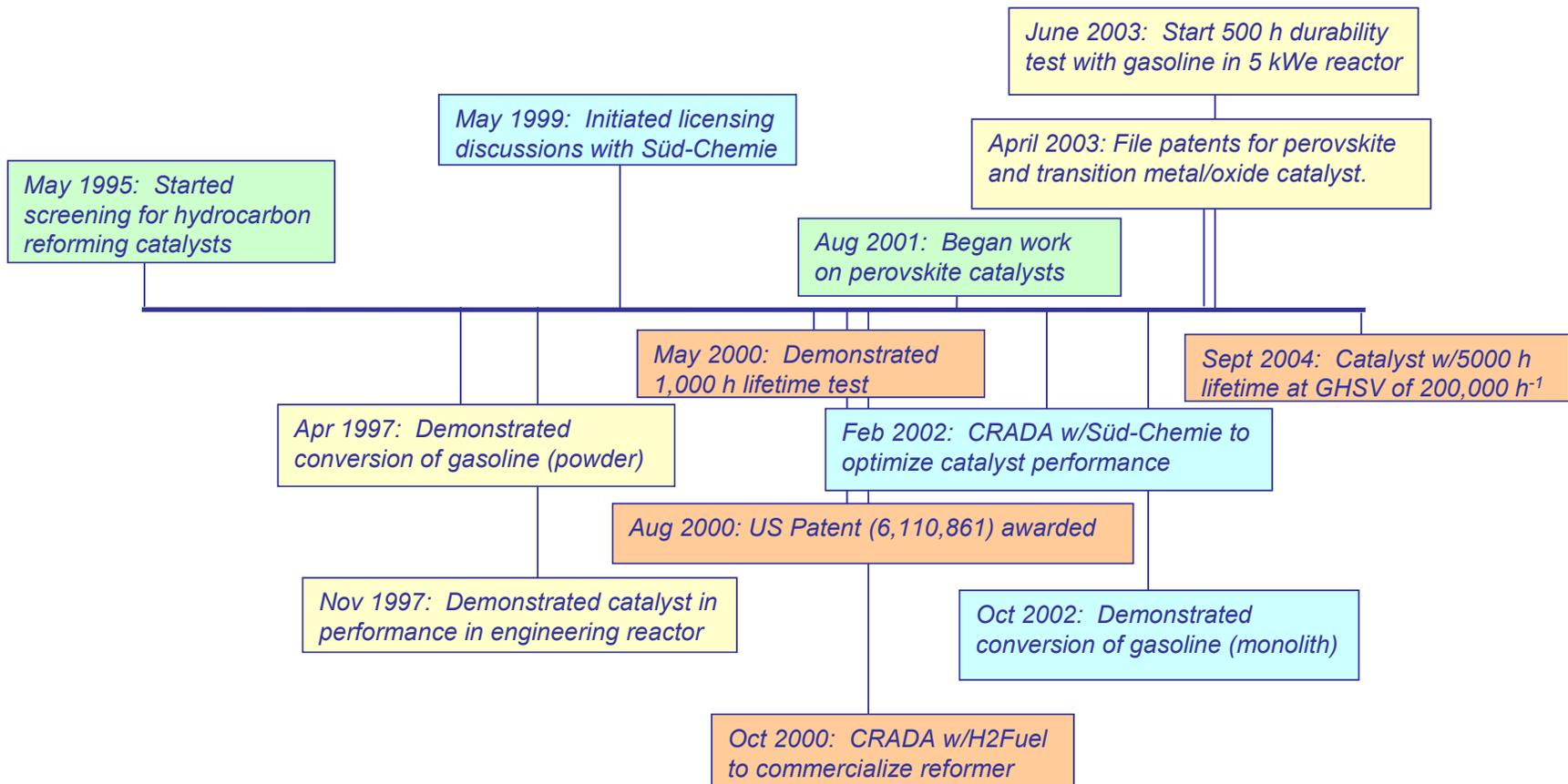
- Detailed knowledge of reaction process would be helpful.

*Using the Advanced Photon Source at ANL, we are studying reaction and catalyst deactivation mechanisms. Through university collaboration, catalyst characterization and kinetic/mechanistic studies are being conducted.*

# Project timeline

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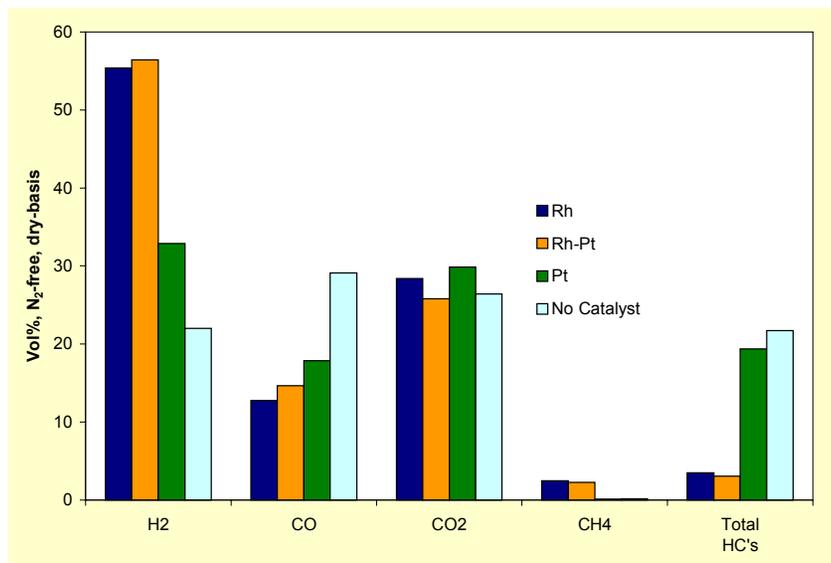
# *FY2003 accomplishments*

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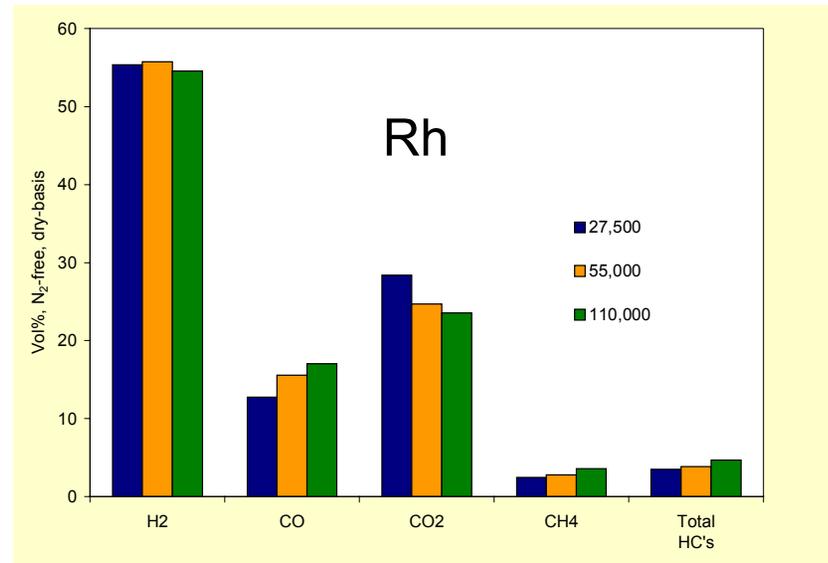
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- For transition metal on mixed oxide supports
  - ✓ Began testing monoliths with commercial grade gasoline
  - ✓ Demonstrated 55% H<sub>2</sub> (dry, N<sub>2</sub>-free) from sulfur-free (<450 ppb S) gasoline at GHSV of 110,000 h<sup>-1</sup>
  - ✓ Identified mechanisms for catalyst deactivation
  - ✓ Identified new oxide substrate that is more stable than ceria under reforming conditions
- For the Ni-based perovskites
  - ✓ Began testing powders with commercial grade gasoline
  - ✓ Optimized composition to improve structural stability while maintaining high activity
  - ✓ Demonstrated <50% loss in activity with benchmark fuel w/50 ppm S
- Filed two patent applications

# Rh catalysts produced reformat with high H<sub>2</sub> concentration from sulfur-free gasoline



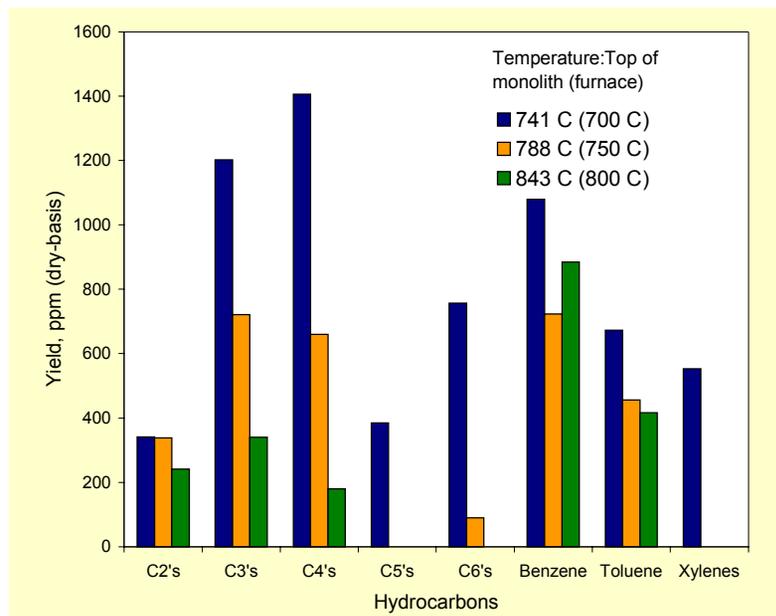
Fuel: Chevron-Phillips No-Sulfur Gasoline (<450 ppb S)  
Feed ratio: O<sub>2</sub>:C = 0.5, H<sub>2</sub>O:C = 1.8, GHSV = 27,000 h<sup>-1</sup>,  
Furnace Temperature is 700°C.



Fuel: Chevron-Phillips No-Sulfur Gasoline (<450 ppb S)  
Feed ratio: O<sub>2</sub>:C = 0.5, H<sub>2</sub>O:C = 1.8, Furnace  
Temperature is 700°C.

- Rh and Rh-Pt catalysts produced a reformat containing  $\geq 55\%$  H<sub>2</sub> (N<sub>2</sub>-free, dry-basis) at a GHSV of 27,000 h<sup>-1</sup>.
- 55% H<sub>2</sub> concentration was maintained at a GHSV of 110,000 h<sup>-1</sup> for Rh.

# For Rh, non-CH<sub>4</sub> hydrocarbon slip decreased with increasing temperature (gasoline)

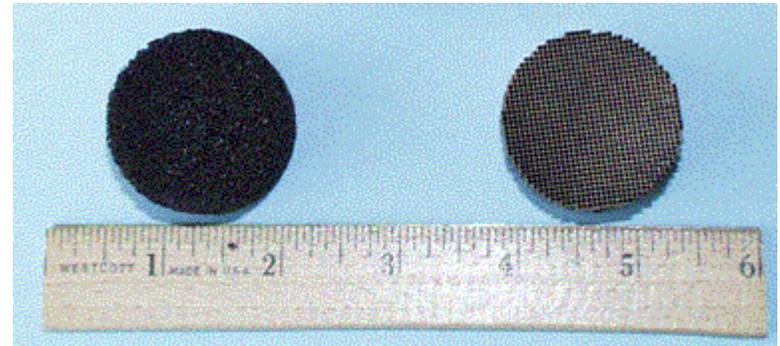


Fuel: Chevron-Phillips No-Sulfur Gasoline (<450 ppb S)  
Feed ratio: O<sub>2</sub>:C = 0.5, H<sub>2</sub>O:C = 1.8, GHSV = 55,000 h<sup>-1</sup>

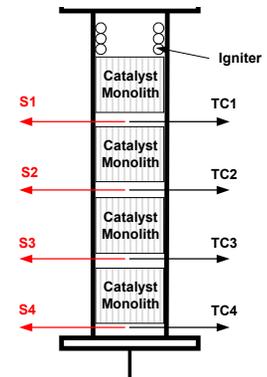
- Increasing the O<sub>2</sub>:C ratio to increase the reaction temperature results in a decrease in the H<sub>2</sub> yield.
- Raising the reaction temperature accelerates the rate of catalyst deactivation.

## Tests are in progress to determine the optimal geometry for the structured support to improve fuel efficiency

- High mass transfer rates will be crucial in operating at a GHSV of  $200,000 \text{ h}^{-1}$
- We are evaluating the performance of the catalyst supported on different structured forms
  - ✓ monoliths with 600, 900, and 1200 cpsi
  - ✓ metal foams
- Testing is being done in a  $\text{kW}_e$  reactor system under adiabatic conditions

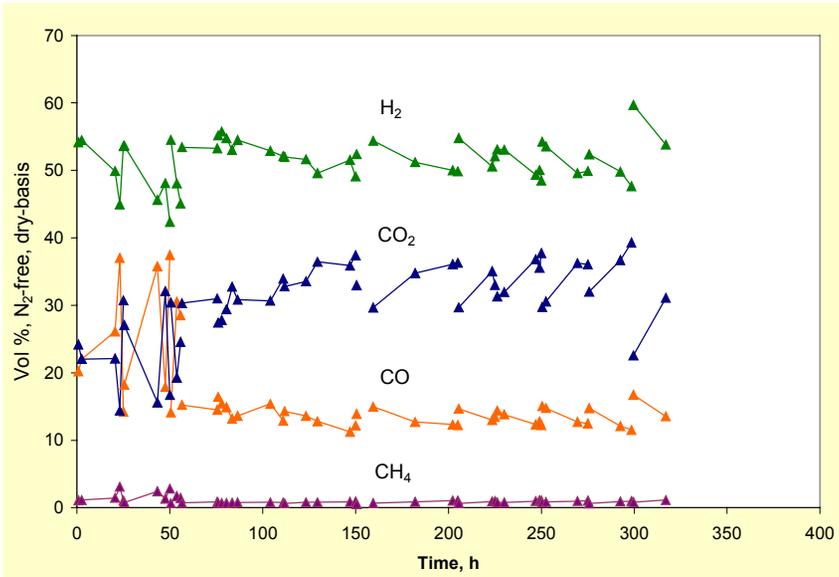


Metal foam (left) and 600 cpsi monolith



$\text{kW}_e$  Reactor System

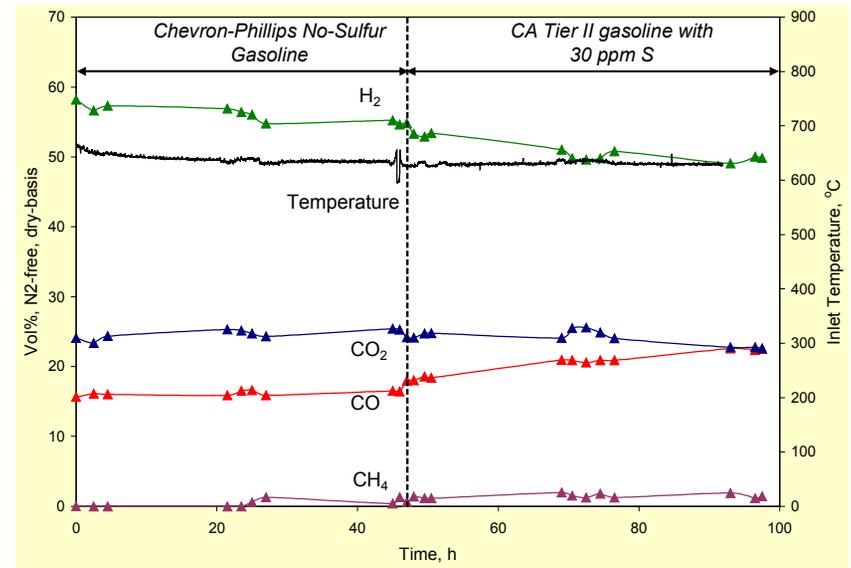
# Deactivation and sulfur poisoning observed in long-term tests with Pt-Rh catalyst



Periodic Shutdown/Restart

Fuel: Sulfur-free benchmark fuel (75 vol% isooctane, 19 vol% xylenes, 5 vol% methylcyclohexane, x% 1-pentene)  
Feed ratio: O<sub>2</sub>:C = 0.41, H<sub>2</sub>O:C = 1.6, GHSV = 9,000 h<sup>-1</sup>

- Activity loss during operating cycle was mostly recovered on restart for testing involving periodic shutdown.
- Greater loss of activity due to sulfur poisoning than deactivation for testing involving continuous operation.

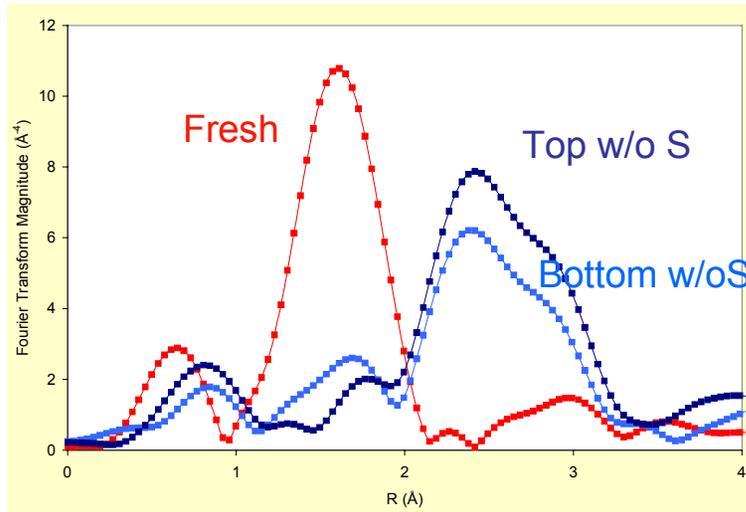


Continuous Operation

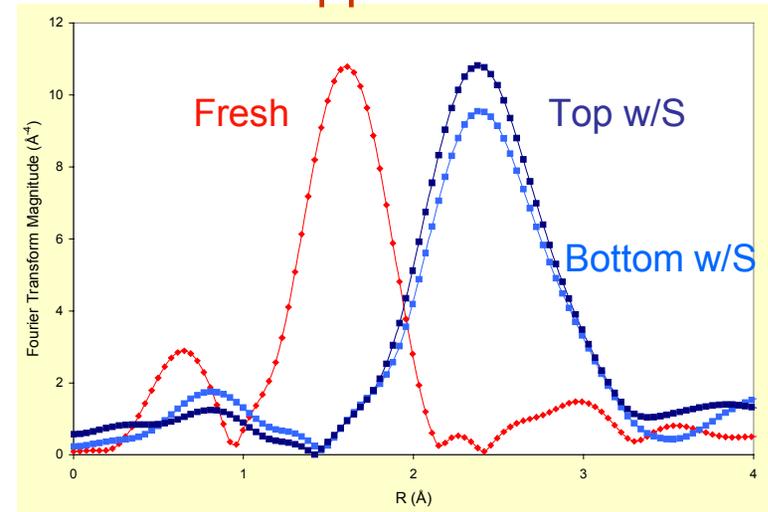
Fuels: Chevron-Phillips No-Sulfur Gasoline (<450 ppb S), CA Tier II w/30 ppm S  
Feed ratio: O<sub>2</sub>:C = 0.45, H<sub>2</sub>O:C = 1.6, GHSV = 57,000 h<sup>-1</sup>

# EXAFS showed that Pt sinters during reforming and that sulfur may further promote sintering

No Sulfur



50 ppm Sulfur



Sample	Shell	N	$\Delta s^2 \times 10^4 (\text{\AA}^2)$	R ( $\text{\AA}$ )	$\Delta E$ (eV)	$\rho$ (%)
Fresh	Pt-O	6.0	0.0	2.07	0.1	2.3
Bottom - w/o S	Pt-O	1.7	0.3	2.10	0.0	6.2
	Pt-Pt	7.3	0.0	2.78	0.0	
Top - w/o S	Pt-O	1.0	0.2	2.14	0.4	3.8
	Pt-Pt	9.6	0.0	2.78	0.0	
Bottom - w/S	Pt-O	1.5	0.0	2.29	11.3	3.9
	Pt-Pt	10.5	0.1	2.76	0.0	
Top - w/S	Pt-O	1.4	0.0	2.29	10.8	6.3
	Pt-Pt	12.0	0.0	2.76	0.2	

- EXAFS analysis is on going for Rh and Pt-Rh catalysts.

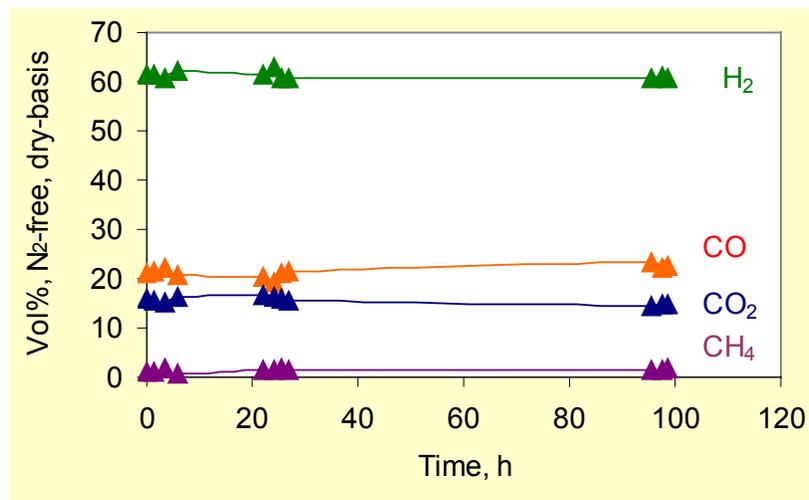
# Sintering of ceria substrate shows need for more stable substrates

- Because of concern over loss of activity due to sintering of the ceria, we are investigating more thermally-stable supports.

	Surface Area (m <sup>2</sup> /g)		
	As prepared	ATR (150 h)	Thermal Treatment*
Rh/doped -CeO <sub>2</sub>	36	17	3
Rh/MO	37	33	33

\* 24-h at 900°C in 33% H<sub>2</sub>, 17% H<sub>2</sub>O, bal N<sub>2</sub>

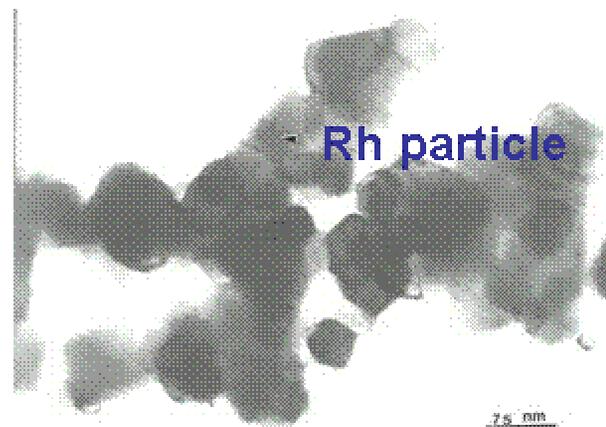
- Rh/MO showed stable yields of H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub> over 100 h reforming sulfur-free benchmark fuel.



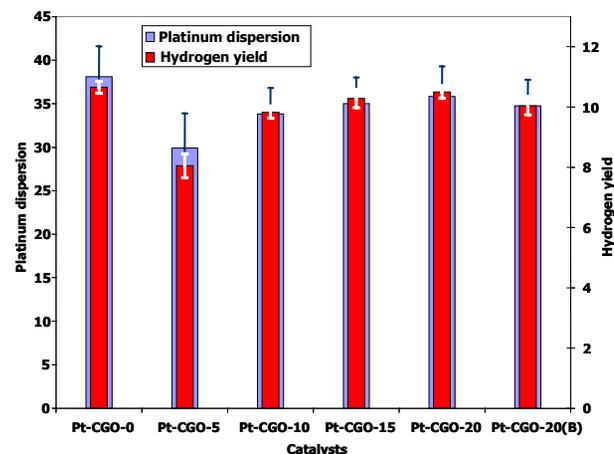
Conditions: Benchmark fuel, O<sub>2</sub>:C = 0.45, H<sub>2</sub>O:C = 1.6, GHSV = 82,000 h<sup>-1</sup>

# Some highlights from our collaborations with the University of Alabama

- TEM study to determine the effect of H<sub>2</sub> reduction on Rh particles and ceria grains.
  - ✓ Significant increase in ceria grain size after reduction
  - ✓ Sharp interface between Rh and ceria observed on calcined samples becomes diffuse after reduction suggesting poorer interaction between metal and ceria
- Kinetic study of isobutane steam reforming catalyzed by PtCe<sub>1-x</sub>Gd<sub>x</sub>O<sub>2-(x/2)</sub>
  - ✓ Rate is proportional to Pt dispersion
  - ✓ Effect of Gd concentration over the range of 0 ≤ x ≤ 0.2 is minimal
  - ✓ A rate equation based on the Langmuir-Hinshelwood-Watson kinetic model has been developed



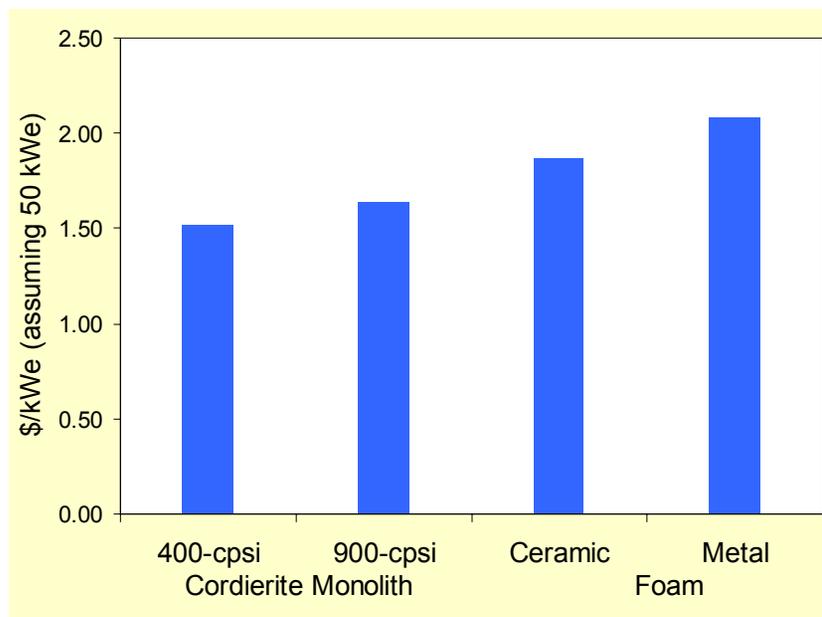
2 wt% Rh-CGO after reduction



Relationship between Pt dispersion and H<sub>2</sub> yield for Pt-CGO at different Gd concentrations

# Cost targets can be achieved

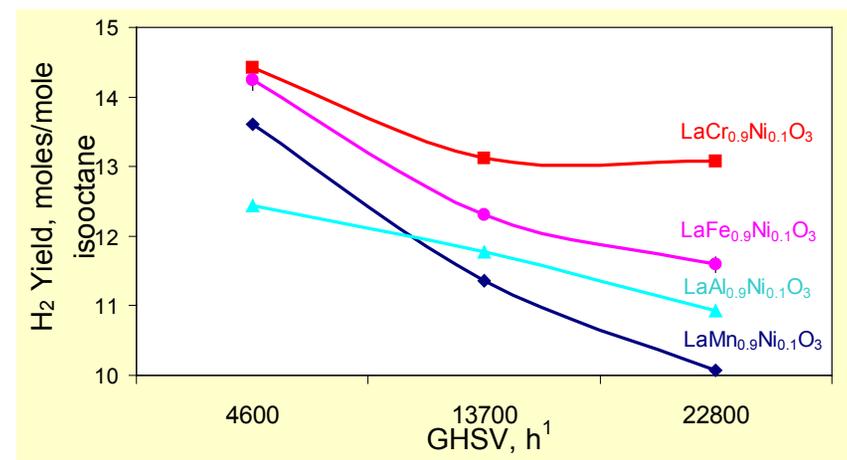
- With a GHSV of  $200,000 \text{ h}^{-1}$ , the cost target of  $\leq \$5/\text{kWe}$  is achievable, even with a precious metal catalyst.
- The estimated materials cost (structure, oxide substrate, precious metal), not including manufacturing cost, is  $\$1.50\text{-}\$2.50/\text{kWe}$ .



# We have focused on increasing the stability of Ni-based perovskites

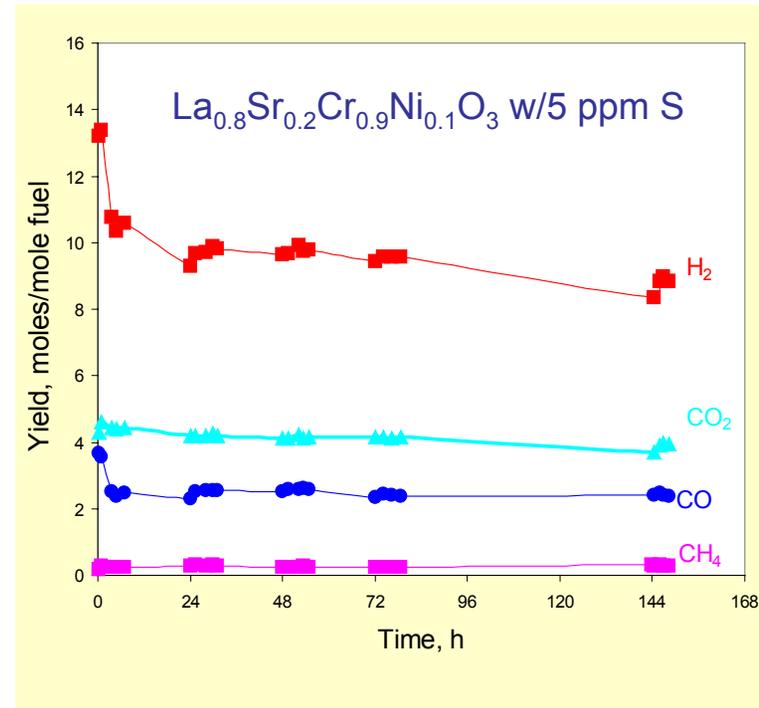
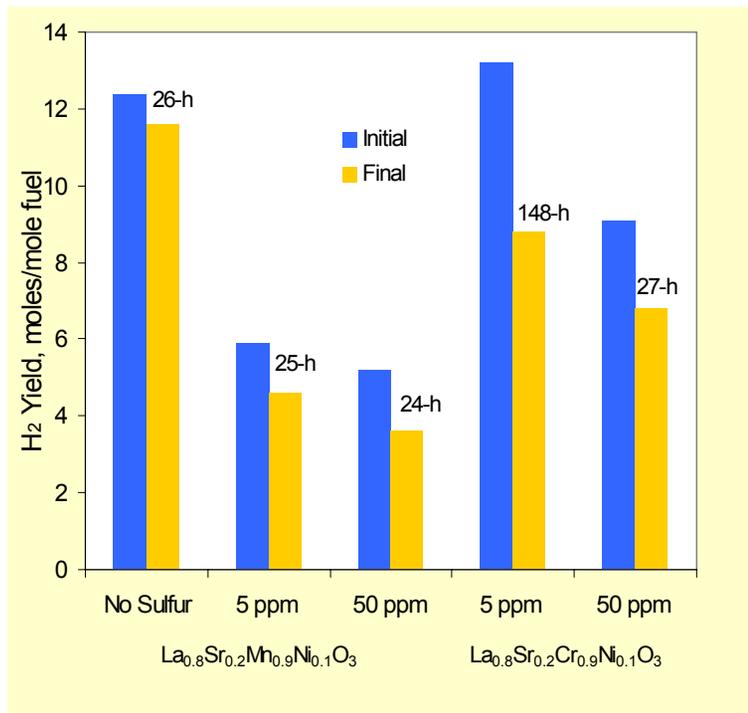
- Lanthanum on the A-site of  $\text{ACr}_{0.9}\text{Ni}_{0.1}\text{O}_3$  gave the best performance in terms of  $\text{H}_2$  yield, fuel conversion, and avoiding coke formation.
- Cr was the best dopant on the B-site of  $\text{LaB}_{0.9}\text{Ni}_{0.1}\text{O}_3$  for stabilizing the perovskite structure while maintaining high reforming activity.

A-site	$\text{H}_2$ Yield*	Conv., %	C, Wt%
La	13.1	96.9	0.63
Pr	11.3	87.6	2.2
Nd	11.9	97.0	6.3
Gd	13.3	99.9	5.1
Er	13.9	97.7	8.0



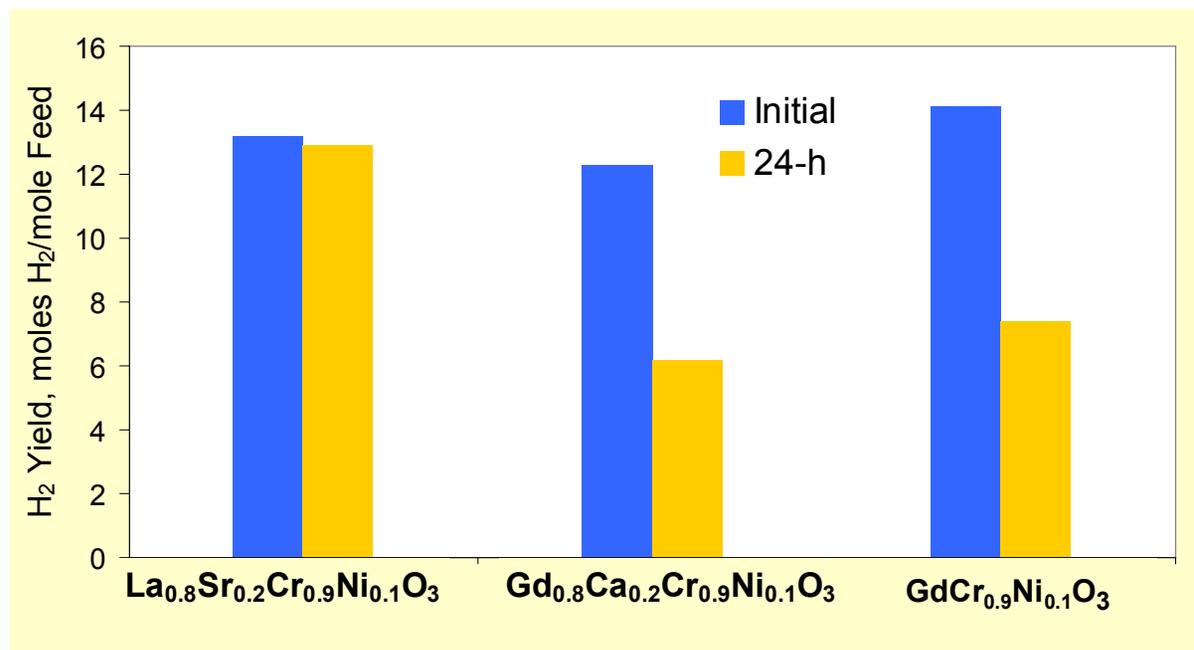
Fuel: Isooctane, Feed ratio: Temperature = 700°C,  $\text{O}_2:\text{C} = 0.37$ ,  $\text{H}_2\text{O}:\text{C} = 1.15$ ,  $\text{GHSV} = 22,800 \text{ h}^{-1}$

# Perovskites are susceptible to sulfur poisoning with most activity lost during the first 10 h



Fuel: Benchmark fuel (78 vol% isooctane, 16 vol% xylenes, 5 vol% methylcyclohexane, 1% 1-pentene) with sulfur added as benzothiophene  
Feed ratio: Temperature = 700°C, O<sub>2</sub>:C = 0.45, H<sub>2</sub>O:C = 1.6, GHSV = 25,000 h<sup>-1</sup>

# $La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$ exhibited <5% loss in $H_2$ yield over 24-h in test with sulfur-free gasoline



Fuels: Chevron-Phillips No-Sulfur Gasoline (<450 ppb S)  
Feed ratio: O<sub>2</sub>:C = 0.45, H<sub>2</sub>O:C = 1.6, GHSV = 25,000 h<sup>-1</sup>

# FY2003 milestones

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<u>Milestone</u>	<u>Date</u>
Demonstrate 60% H <sub>2</sub> from California Tier II low sulfur gasoline at 700-800°C and a space velocity of 100,000 h <sup>-1</sup> with structured form of metal-doped ceria or perovskite catalyst (N <sub>2</sub> , H <sub>2</sub> O-free basis).	02/03

*Demonstrated 55% H<sub>2</sub> from no sulfur gasoline at 110,000 h<sup>-1</sup> in a microreactor. Testing with gasoline with 30 ppm sulfur to be conducted in 5-kWe adiabatic reactor.*

Demonstrate improved sulfur tolerance of non-Pt catalysts with benchmark fuel containing 30 ppm S (less than 50% loss in activity over a 100-h period compared to activity measured with sulfur-free benchmark fuel.)	06/03
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*In progress – Less than 50% loss in H<sub>2</sub> yield over 24-h.*

# Future work

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- Evaluate catalyst performance on a larger scale using 1-5 kWe adiabatic reactors.
  - ✓ Confirm microreactor results
  - ✓ Better evaluate long-term performance
  - ✓ Determine optimal geometry for structured support
- Work to decrease precious metal loading while improving catalyst stability and sulfur tolerance.
- Work to improve catalyst activity and sulfur tolerance of perovskite catalysts.
- Address the effect of rapid startup on catalyst stability.
- Increase our fundamental understanding of reaction processes and mechanisms for deactivation and sulfur poisoning.